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DUROMETRY AS A DIAGNOSTIC TOOL IN CASTABLE URETHANE TECHNOLOGY

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Abstract

Probably no other property of a cast elastomer is more widely cited than its durometer. The problem is that a single measurement made at room temperature after cure does not always verify quality. But if done systematically, hardness measurement can be used as an inexpensive tool for quality control and quick diagnosis of certain problems. Specifically, this paper shows how prepolymer heat aging, off-ratio conditions, and incorrect postcure conditions can often be detected by measurement of hardness during cure and at various times and temperatures after cure.

Introduction

In order to increase the amount of useful diagnostic information from durometry, the use of a composite graph, referred to here as a "durometric profile", is suggested. The profile consists of three parts described below. Using only a hardness gauge, a stopwatch, an oven, and possibly a refrigerator, profiles can be constructed under known processing conditions for specific formulations. The profiles can then be saved for future reference to help determine the validity of claims of poorly processed parts, or to help in spot checking production quality, or even to help establish the best processing conditions.

Construction of a Durometric Profile

To construct a profile, take a piece of graph paper and set up as shown in Figure 1. It is not necessary to computer fit the curves; simply connecting measurement points is good enough.

The idea is for the first part of the profile to show the durometer build-up ***during cure***, the second part to show build-up ***after cure***, and the third part to show variation of durometer with ***temperature*** after cure. Although each part of the profile by itself would be expected to give more processing information than a single room temperature measurement taken a few days after cure, the composite profile should further differentiate processing conditions.

Several other comments concerning durometric profile construction should be made. First, although not presented here, it may sometimes be a good idea to plot two points for each measurement, either the high and the low value in order to determine uniformity, or the initial durometer and the durometer after 15 seconds, in order to capture the "drift" characteristic. Secondly, in the third part of the profile, starting hardness measurement at some temperature below ambient, say 35F, may shed light on characteristic cold hardening behavior (also not presented here). Third, it may be possible to accelerate the process by reducing the time allotted for the second part of the profile. In other words, start the third part of the profile as soon as the sample casting cools to room temperature. Possibly even the cool-down time could be accelerated by quenching in water or by quick freezing. Finally, in the present work, hardness measurement was made by two different people, and they differed by about 2 points apart, on average. Nevertheless, it was decided not to adjust for this, in order to keep closer to real-world situations.

Template Chosen for the Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured with BD

Figure 2 shows the template chosen specifically for curing a 6.3% NCO PTMG/MDI prepolymer with BD. The first part of the template allows 145 minutes for hardness build-up during cure, enough time to establish the characteristic build-up even at low stoichiometry and low postcure temperature. The second part of the template allows seven days to establish the characteristic hardness build-up after cure. The third part of the template allows for the establishment of the characteristic softening with temperature.

Target Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured with BD

Figure 3 shows the target. In other words, with prepolymer in good condition, correct prepolymer temperature, correct stoichiometry, and correct postcure temperature, this is the shape of the composite profile.

All measurements for the first part of the profile were made with the part in the oven. A stopwatch was started after the BD was added; and after being poured, the parts were placed in the oven and remained there for 16 hours (cure and postcure temperature were the same).

For the second part of the profile, the first measurement was always made just before the part was taken out of the postcure oven (16hrs after adding the curative and starting the stop watch), the second after allowing the part to sit at room temperature for two hours (18 hours after starting stopwatch), and the others at several times during the seven days allotted to establish the characteristic build-up.

For the third part of the profile, hardness measurements were taken at room temperature (always assumed to be 70F), 158, 212, 240, and 270F.

Let us now look at how deviations from desired processing conditions change the shape of the profile.

Effect of Prepolymer Condition and Catalyst

Figure 4A shows that decreasing prepolymer temperature from 200F to 165F or slightly catalyzing the BD have little effect. (Of course, a highly catalyzed system would have a much greater effect, but then we would be looking at a different set of reference profiles.) A different batch of prepolymer, slightly wet and gassy with a lower %NCO, caused a more rapid build-up in the first part of the profile and a slight downward displacement of the curves in the second and third parts of the profile. Heat aging also caused a more rapid build-up in the first part of the profile and more of a downward displacement in the second and third parts of the profile.

In contrast to this, Figure 4B shows a second type of chemistry, one where prepolymer heat aging slows hardness build-up in the first part of the profile. This is a **TDI/Ester cured with MBCA**. Note that determination of %chlorine to measure ratio would not have detected this problem.

Effect of Postcure Temperature

Going back to our MDI/PTMG system, Figures 5 A-E, plotted at constant stoichiometry for each profile, show that, above 90% stoichiometry, all three parts of the profile are affected by postcure temperature:

1. The first part of the profile shows that, between 90% and 100% stoichiometry, increasing postcure temperature from 158 to 270F speeds the hardness build-up during cure.

2. The second part of the profile shows several things.

a. Between 90% and 120%, the hardness before the parts are removed from the oven is lowest at 270F.

b. For each postcure temperature, after the parts have been allowed to sit at room temperature for two hours, the hardnesses are almost identical and the next day have all drifted up to the same value again, this change correlating with stoichiometry up to 110%. **The main problem with taking single hardness measurements at room temperature shortly after cure is that processing differences are not obvious.**

c. The lower the postcure temperature, the higher the seven day hardness. (This system actually requires about 14 days for all the hardnesses to reach maximum value.)

3. The third part of the profile shows that thermoplasticity is greatest at the highest postcure temperature. (Note that the starting hardnesses at the beginning of the third part are lower than the ending hardnesses of the second part. The measurements were taken by two different people.)

Effect of Stoichiometry

Looking at the MDI/PTMG system data plotted at constant postcure temperature for each profile, we see from Figures 6 A-D that stoichiometry is definitely the most important variable, affecting hardness variation in all three parts of each profile. **The main value of the durometric profile here is that when we consider the third part of the profile in combination with the first, we see that we can distinguish between high and low stoichiometry.**

Durometric Profile Use in Printing Roll Manufacturing

In Figure 7 the method of presentation is changed to show a composite of three partial durometric profiles for a third type of chemistry, a **TDI/Ester cured with triol**. For each partial profile, each hardness, even the first one, was measured at room temperature at various times after post cure. Some printing roll manufacturers now use such profiles to estimate within a few days after manufacture whether rolls were processed at correct stoichiometry and post cure temperature.

Use of the Profiles to Estimate Actual Processing Condtions of "Unknowns"

Finally, taking one more look at the MDI/PTMG system, it was decided to cast parts under "unknown" processing conditions and use the profiles in Figures 6 A-D to estimate the actual conditions. A technician was asked to cure two parts, choosing within any of these processing conditions: prepolymer temperature 165F - 200F, uncatalyzed or catalyzed BD (at 0.125% level), postcure temperature 158F - 270F, and 80 - 120% stoichiometry. He ran a durometric profile for each, labelled one Unknown #1 (Figure 8), and the other Unknown #2 (Figure 9). These profiles were then used to estimate processing conditions: Low thermoplasticity suggested < 105% theory. The shape of the first part of each profile suggested 90% for #1 and 100% for #2. Use of a transparency to overlay on the reference profiles suggested postcure between 212 and 240F. It was not possible to estimate prepolymer temperature or whether catalyst was used. Final estimates were: 240F postcure and 90-95% stoichiometry for Unknown #1, and 212F postcure and 98 - 103% stoichiometry for Unknown #2. These estimates were correct. Actual conditions were: 190F prepolymer, catalyzed BD, 240F postcure, 90% for Unknown #1; and 195F prepolymer, catalyzed BD, 212F postcure, 100% for Unknown #2.

How to Get the Most Benefit from a Durometric Profile

1. Run reference profiles for your formulation using appropriate variations in stoichiometry, postcure temperature, prepolymer heat aging, and any other variables you think affect your process.

2. Study the profiles to determine which areas give the most processing information at the earliest time in the cure cycle. Use these areas for quick day to day spot checks.

3. Do an occasional complete profile as a spot check.

4. For quality complaints, use part three of the profile to estimate whether ratio was high.

Conclusion

A single room temperature measurement of the hardness of a castable elastomer made within a few days after cure does not always verify quality. But if graphs of hardness build-up during cure, after cure, and at various temperatures after cure are combined into one graph, referred to here as a durometric profile, useful diagnostic information can often be obtained. The profiles generated for this work show sensitivity to stoichiometry, postcure temperature, and prepolymer heat aging.

Acknowledgment

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Abbreviations

MDI	methylene-bis-diphenylisocyanate
TDI	toluene diisocyanate
PTMG	polytetramethylene glycol
BD	1,4-butanediol
TMP	trimethylol propane
TIPA	triisopropanol amine
MBCA	methylene-bis-orthochloroanaline

Figure 1

Master Template for the Construction of a Durometric Profile.

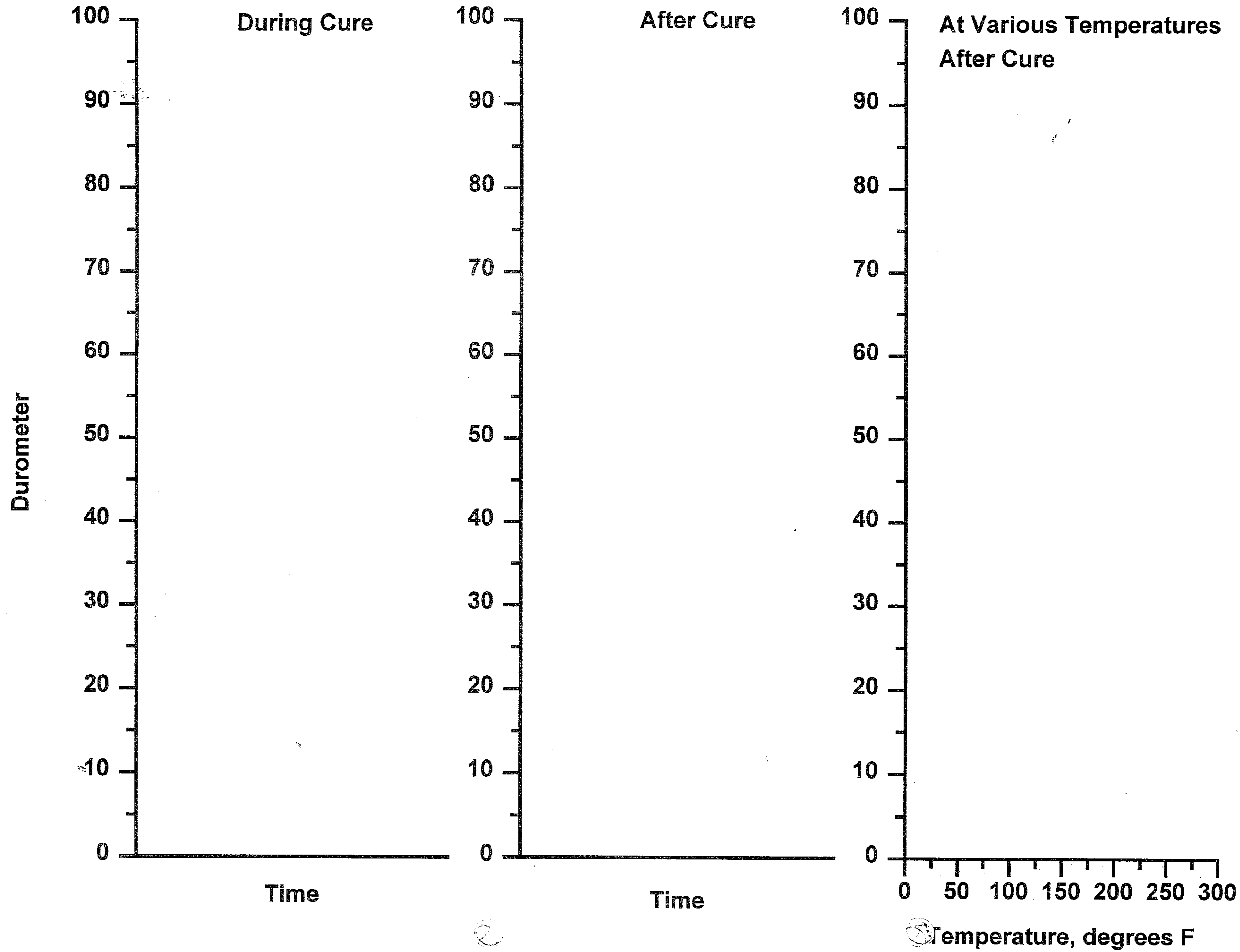
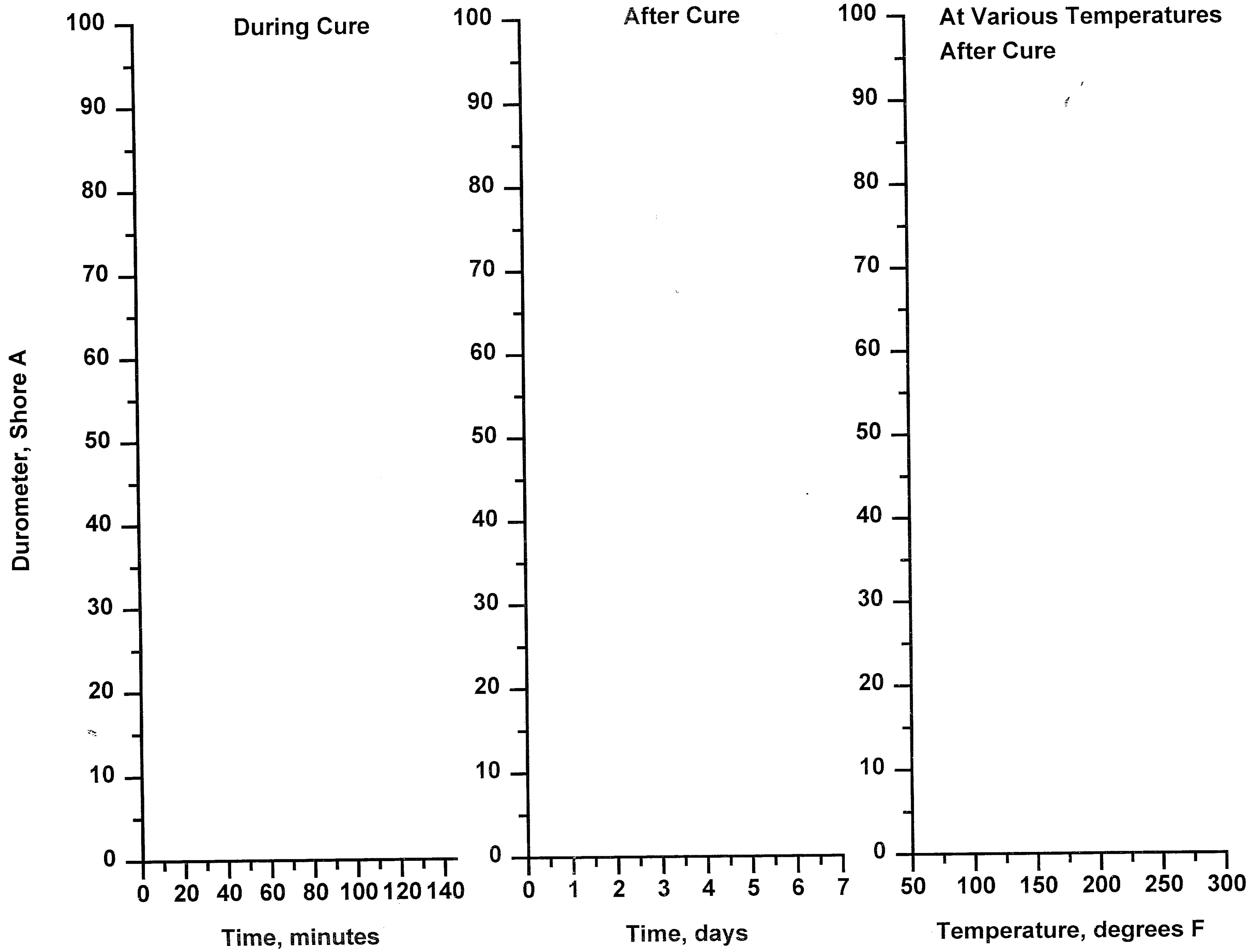


Figure 2

Template Chosen for the Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured with BD.



Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured at 240F at 100% Stoichiometry with BD.
Unaged Prepolymer at 200F. Uncatalyzed BD.

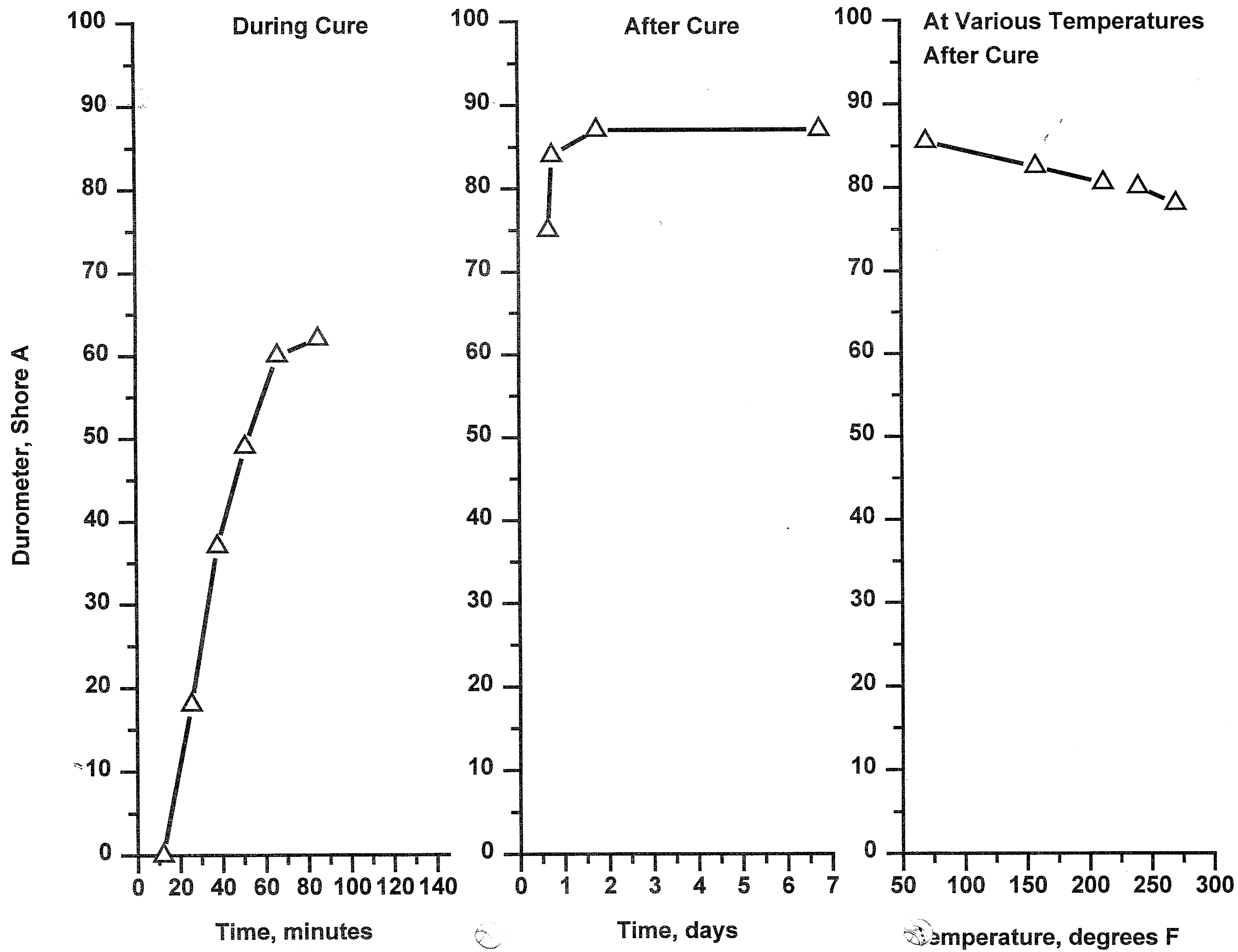


Figure 4A

Durometric Profile of a "6.3"%NCO PTMG/MDI Prepolymer Cured at 240F at "100"% Stoichiometry with BD.

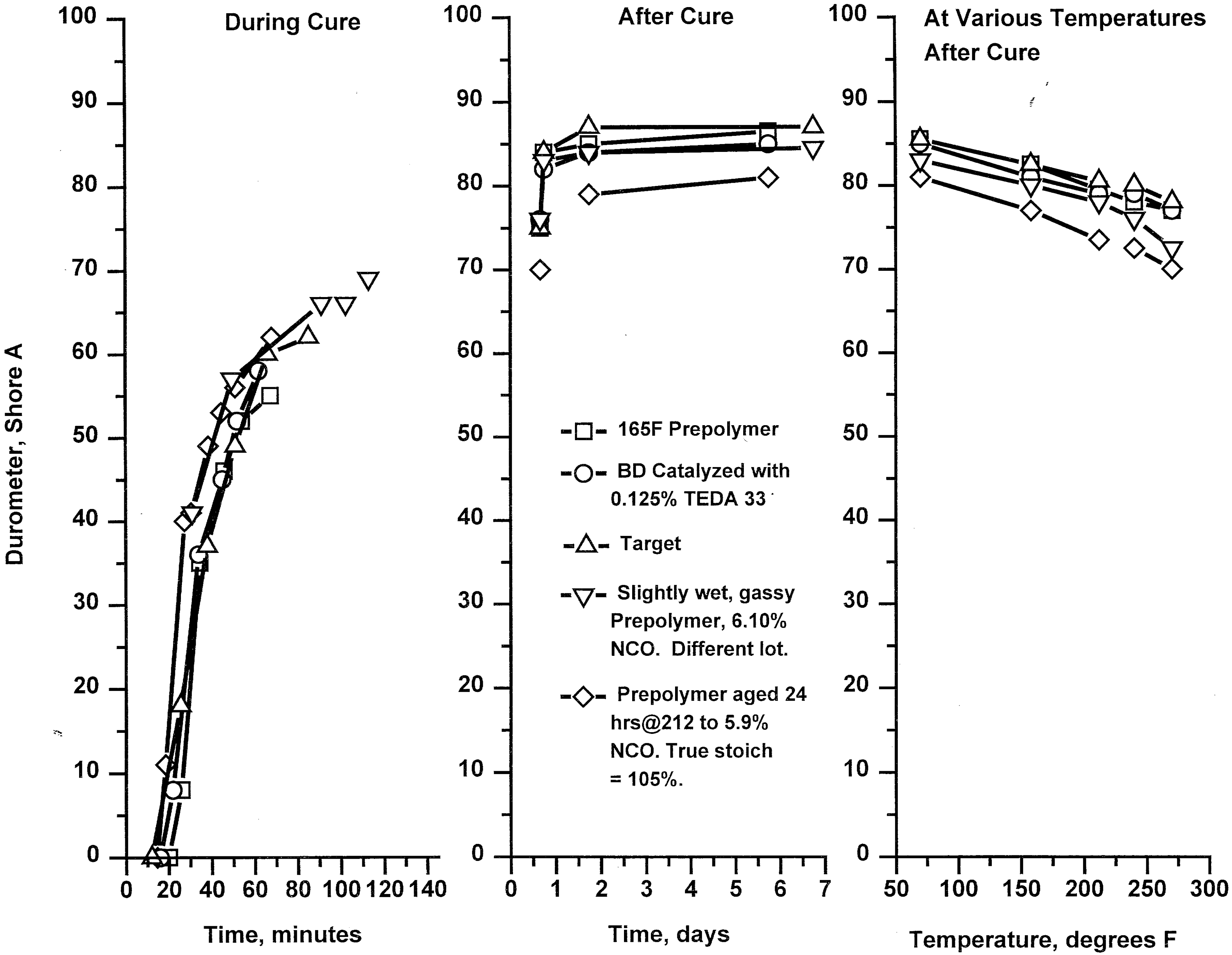


Figure 4B
Durometric Profile of a TDI/Ester Cured at 212F at "100" % Stoichiometry with MBCA

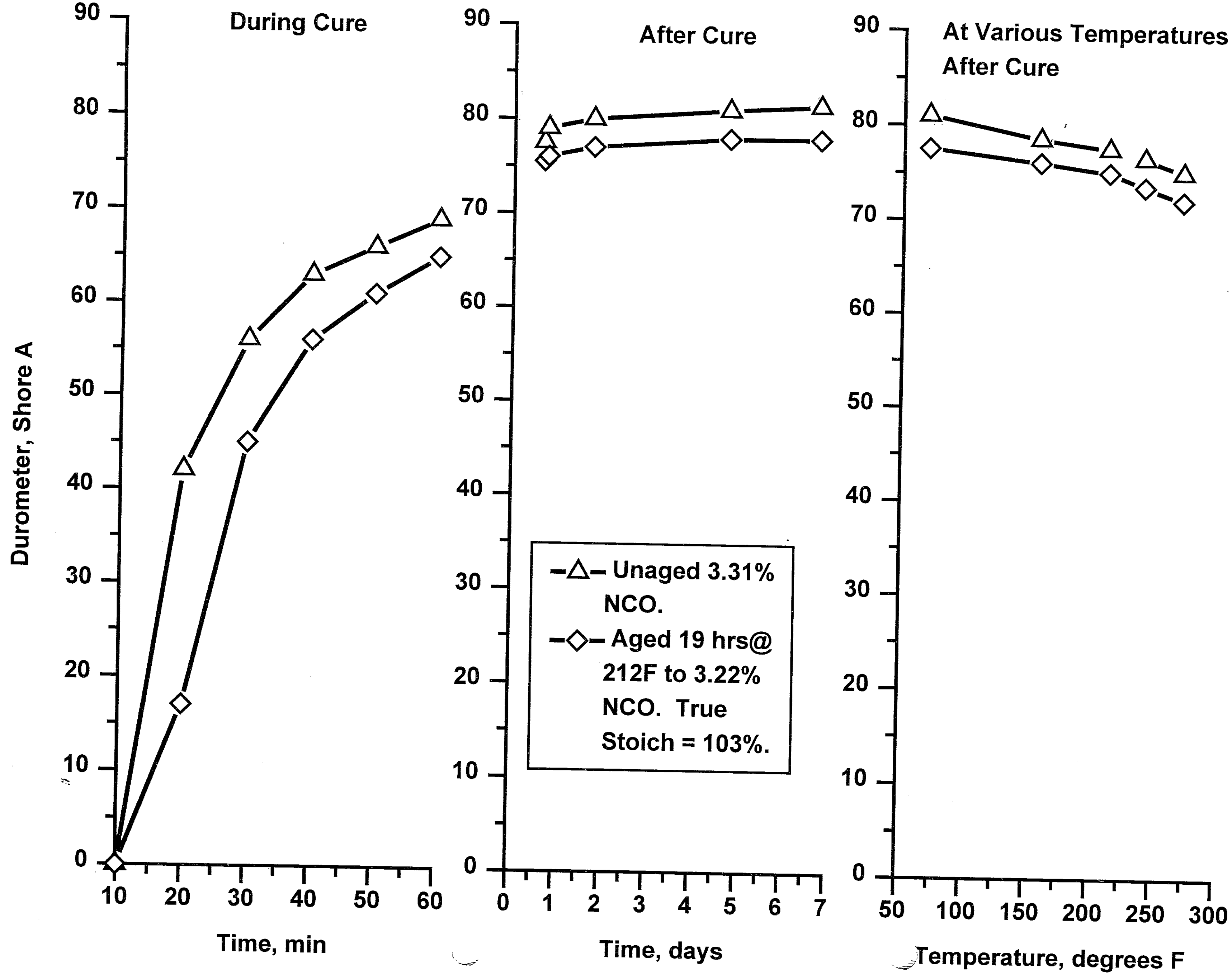


Figure 5A

Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured at Various Temperatures at 80% Stoichiometry with BD. Unaged Prepolymer at 200F. Uncatalyzed BD.

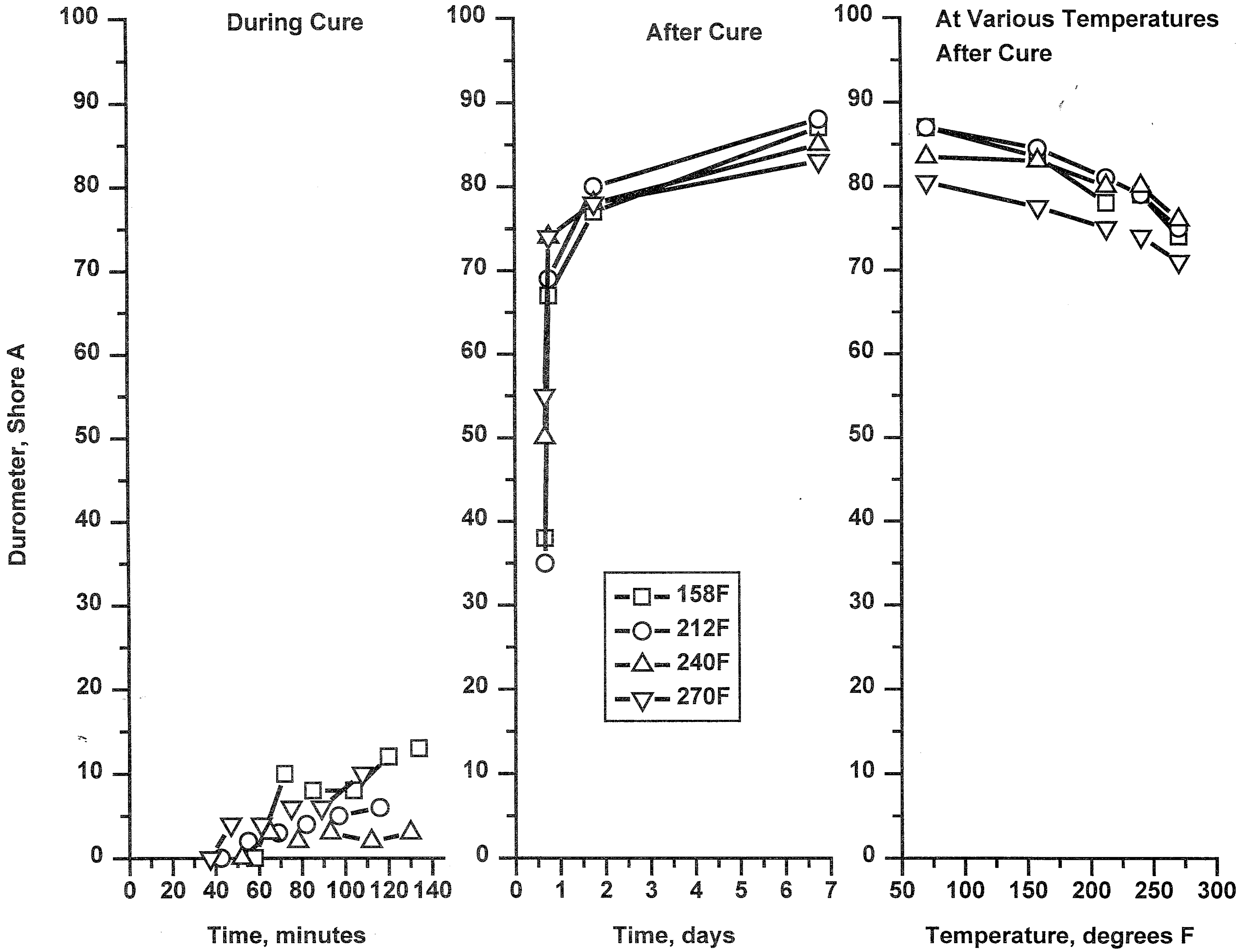


Figure 5B

Durometric Profile of 6.3%NCO PTMG/MDI Prepolymer Cured at Various Temperatures at 90% Stoichiometry with BD. Unaged Prepolymer at 200F. Uncatalyzed BD.

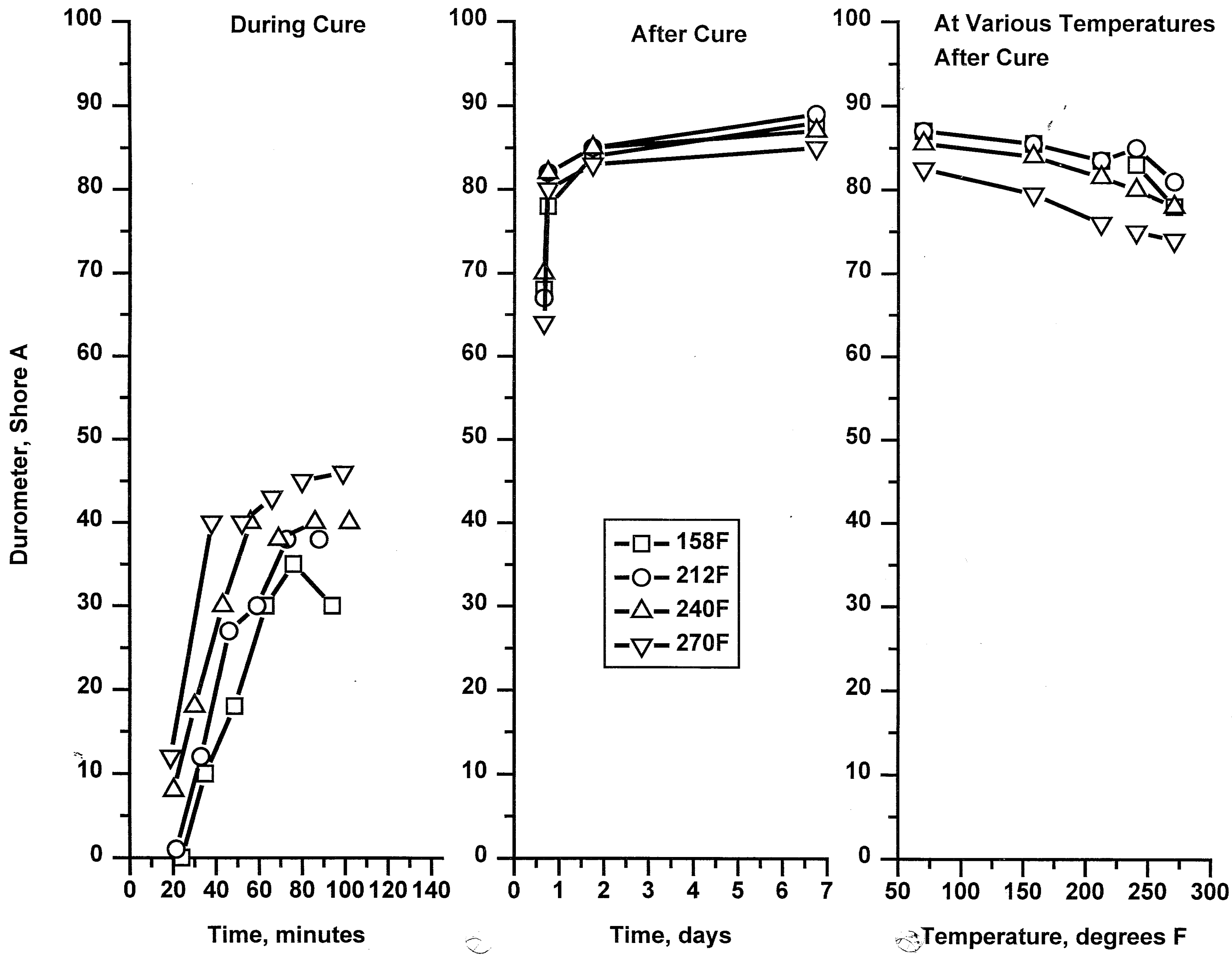


Figure 5C

Durometric Profile of 6.3%NCO PTMG/MDI Prepolymer Cured at Various Temperatures at 100% Stoichiometry with BD. Unaged Prepolymer at 200F. Uncatalyzed BD.

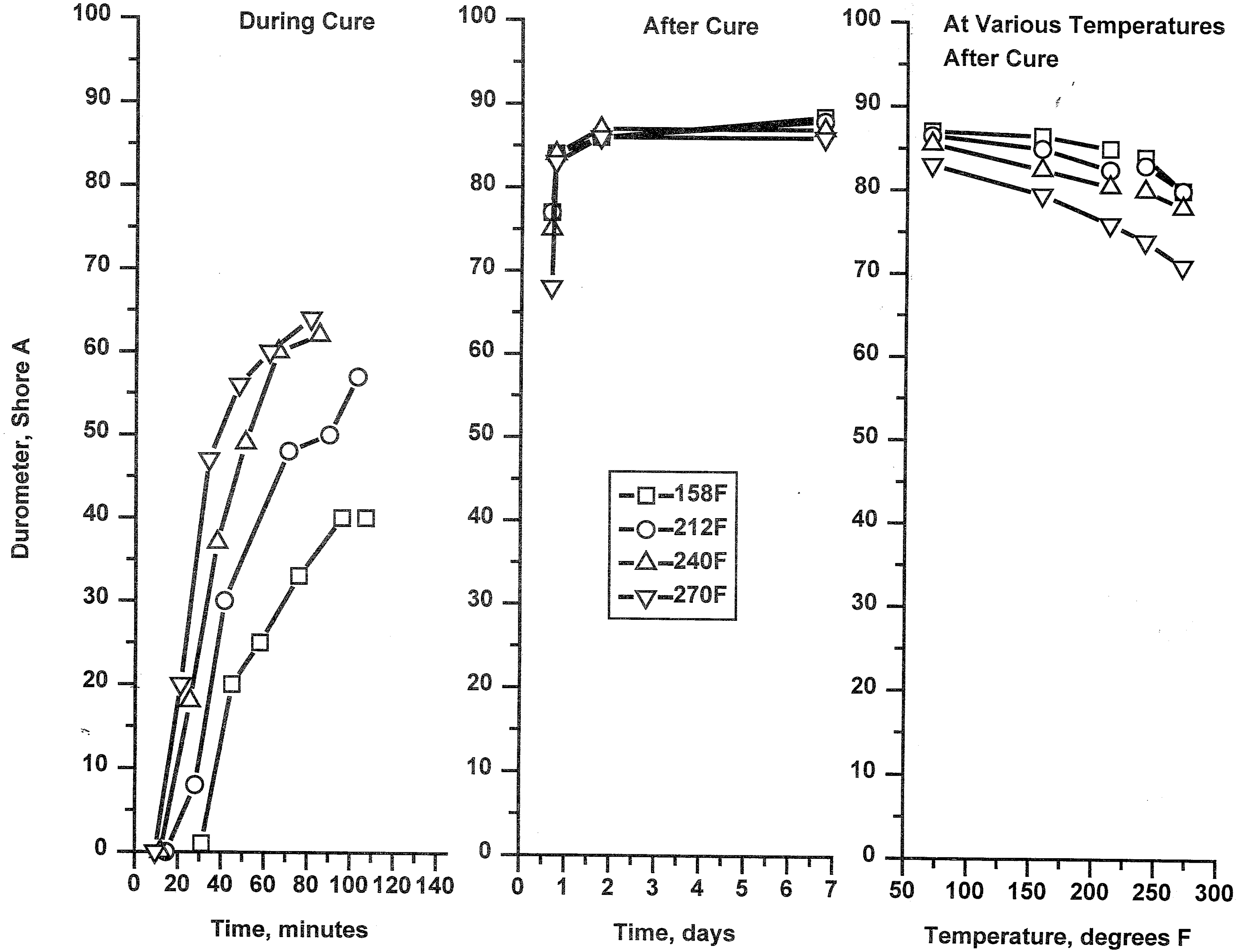


Figure 5D

Durometric Profile of 6.3%NCO PTMG/MDI Prepolymer Cured at Various Temperatures at 110% Stoichiometry with BD. Unaged Prepolymer at 200F. Uncatalyzed BD.

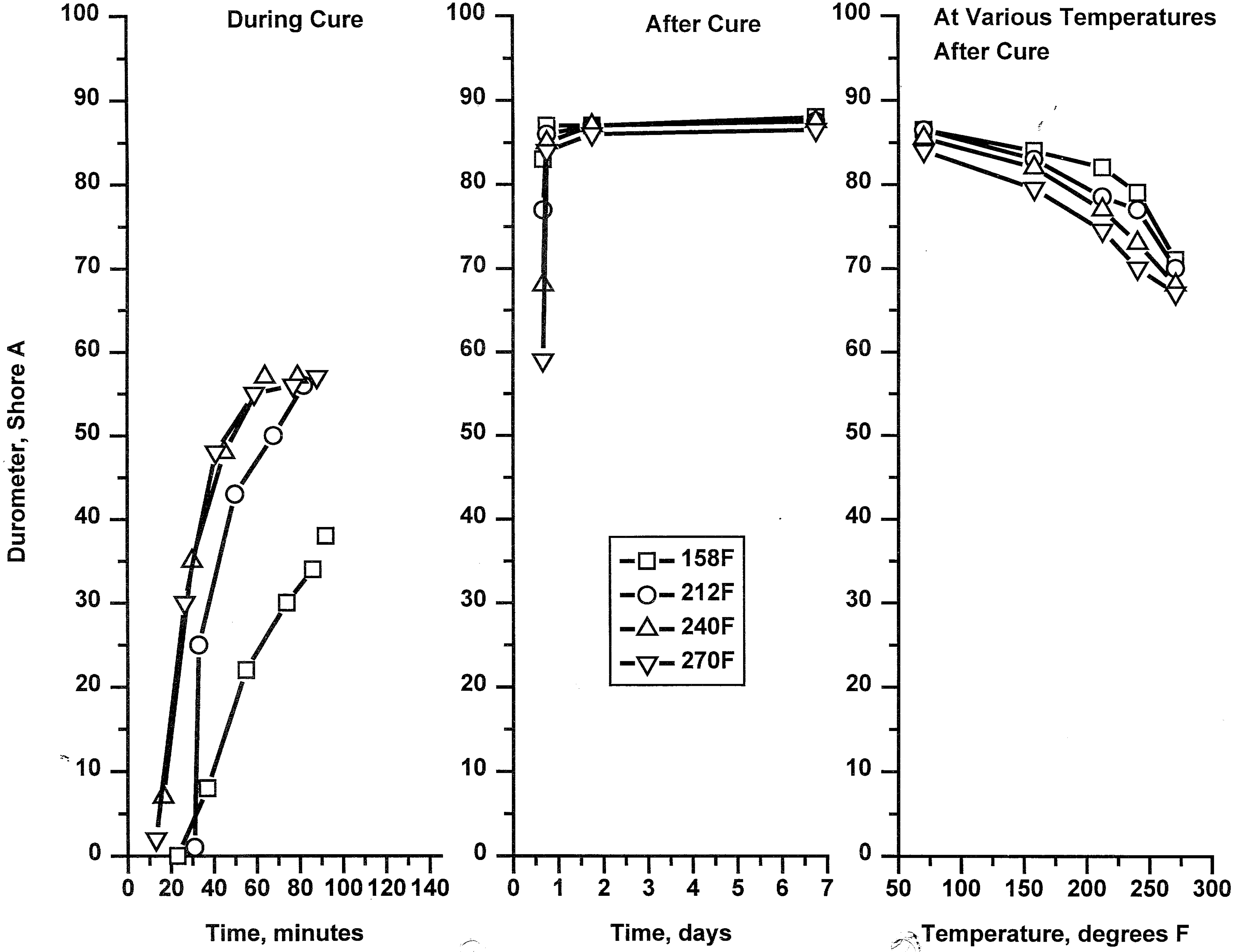


Figure 5E

Durometric Profile of 6.3%NCO PTMG/MDI Prepolymer Cured at Various Temperatures at 120% Stoichiometry with BD. Unaged Prepolymer at 200F. Uncatalyzed BD.

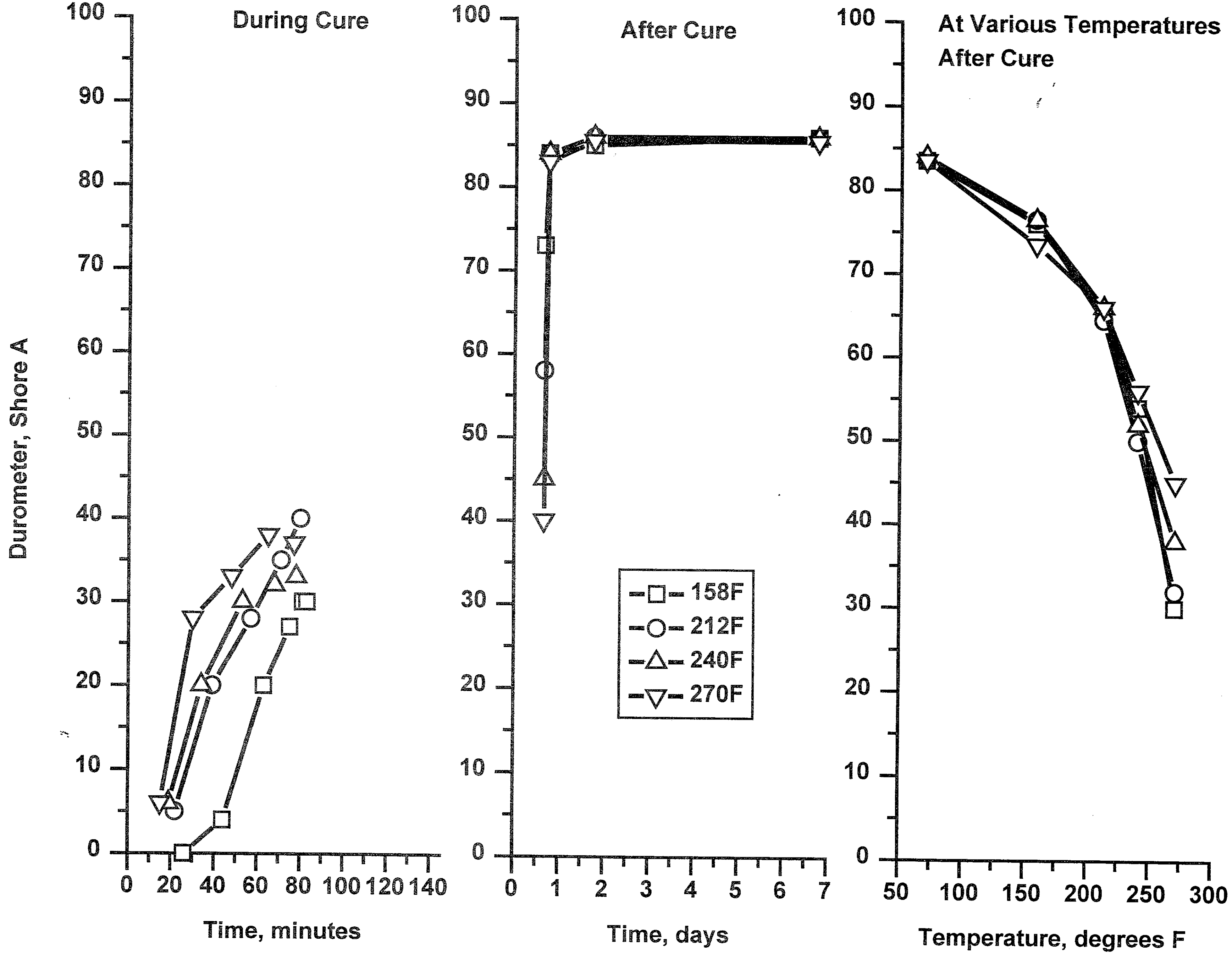


Figure 6A

Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured at 158F at Various Stoichiometries with BD. Unaged Prepolymer at 200F. Uncatalyzed BD.

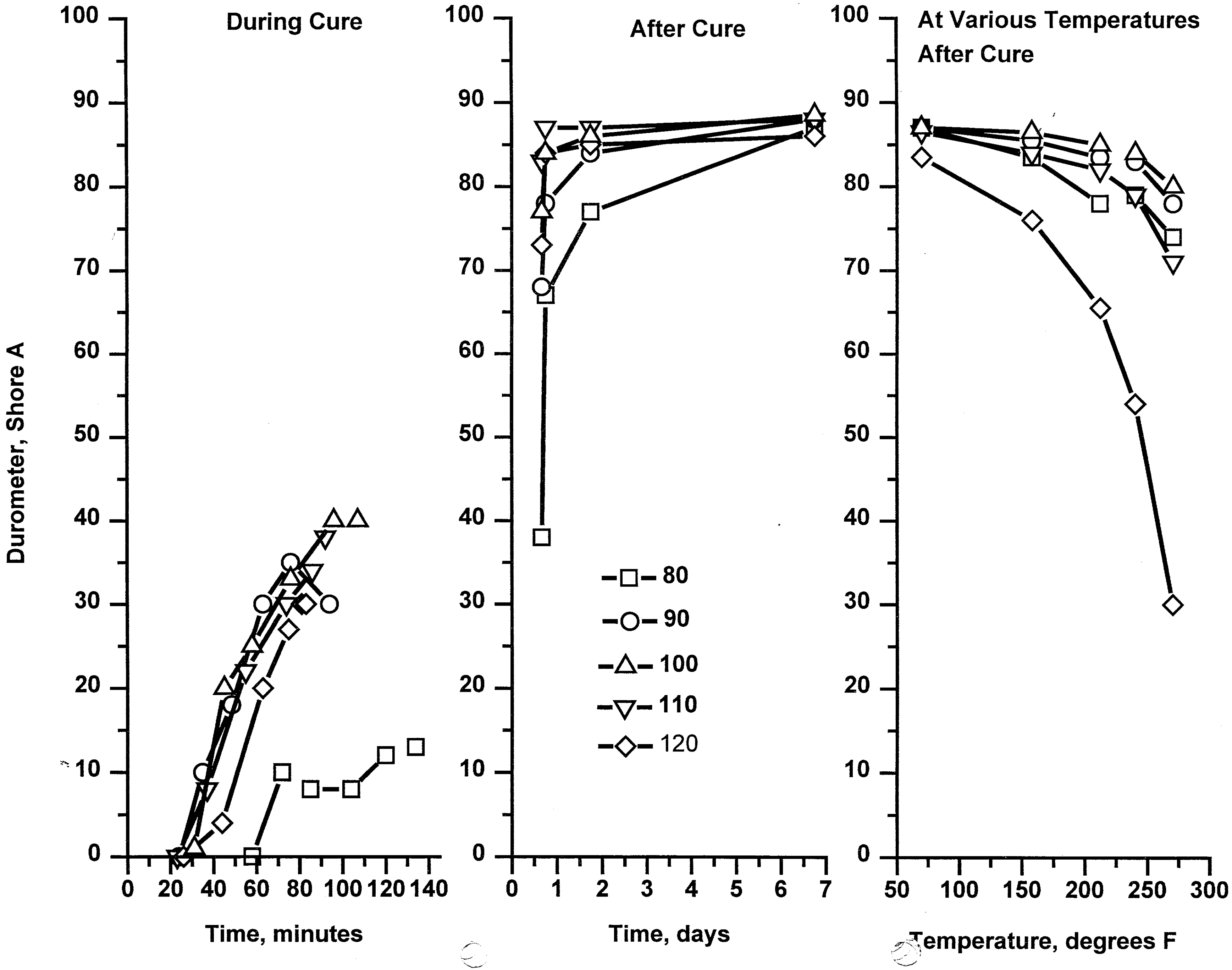
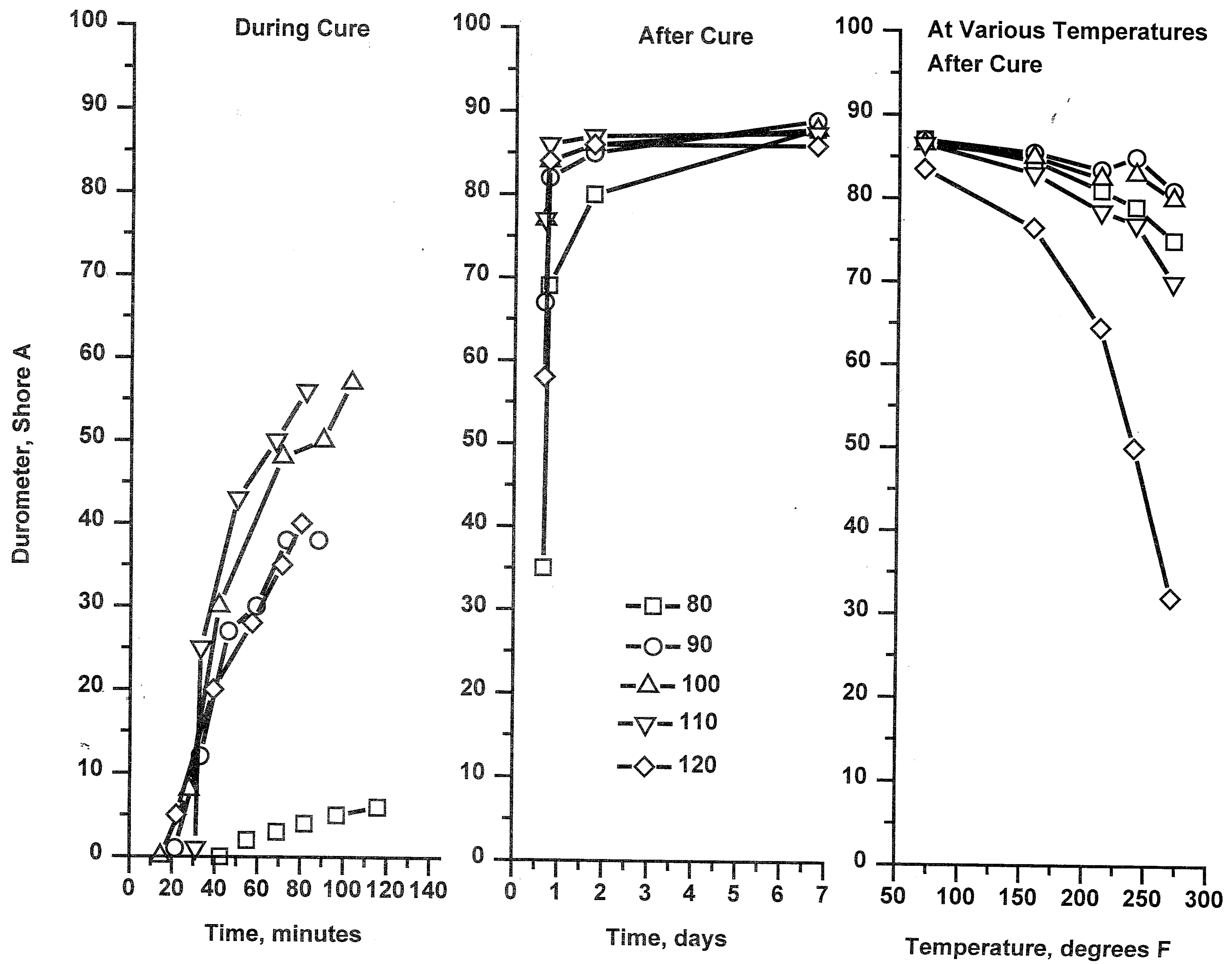


Figure 6B

Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured at 212F at Various Stoichiometries with BD. Unaged Prepolymer at 200F. Uncatalyzed BD.



Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured at 240F at Various Stoichiometries with BD.
Unaged Prepolymer at 200F. Uncatalyzed BD.

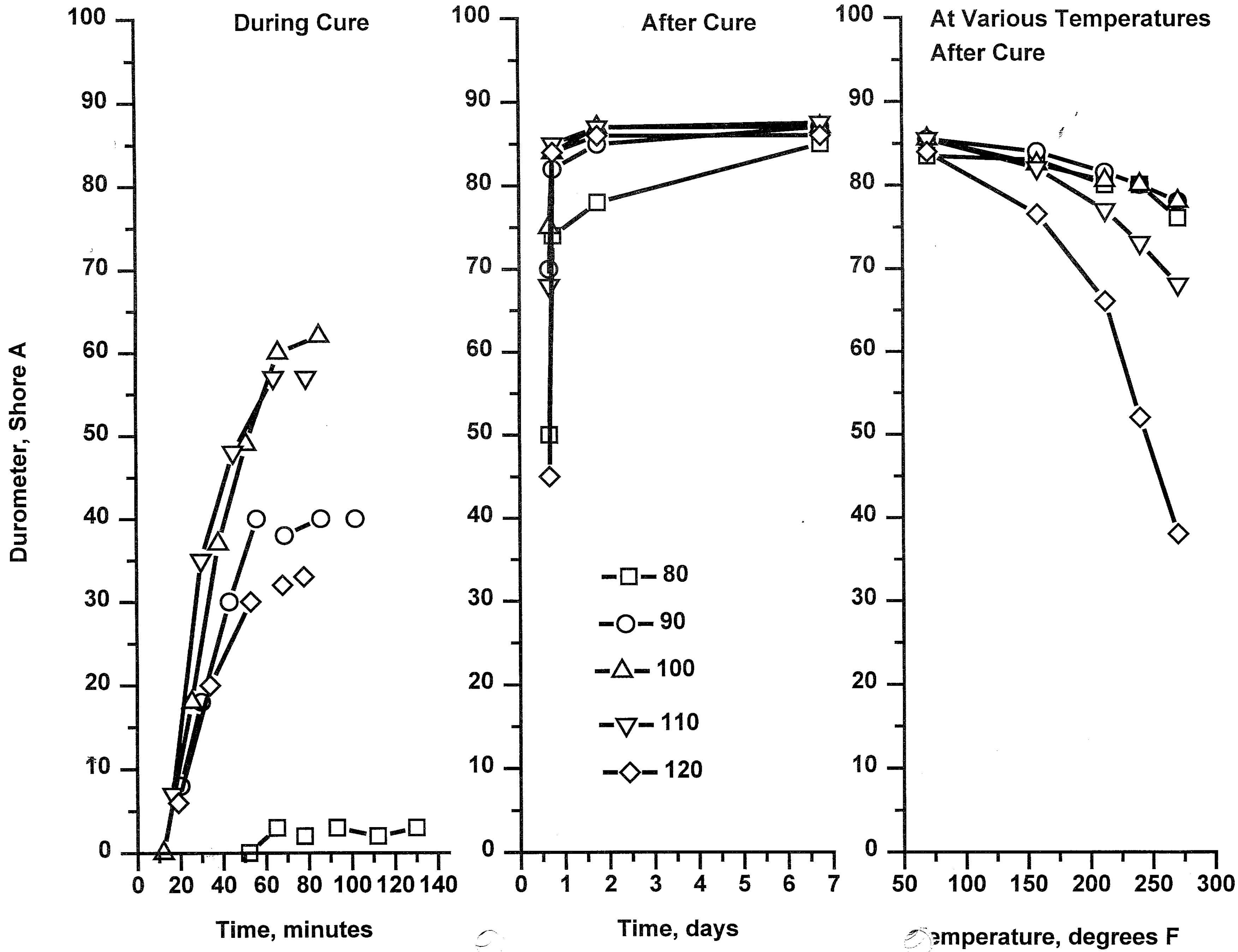
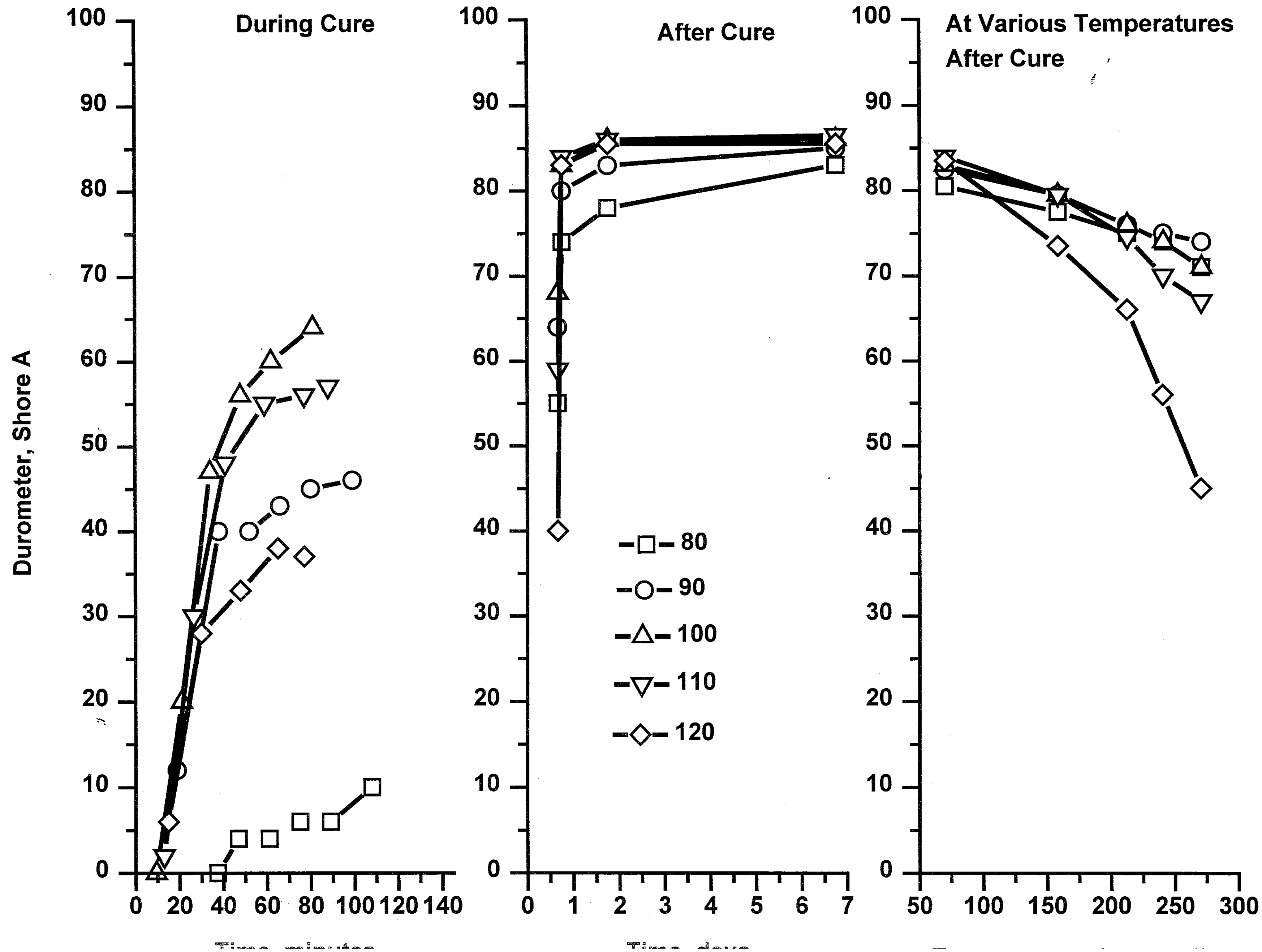


Figure 6D

Durometric Profile of a 6.3%NCO PTMG/MDI Prepolymer Cured at 270F at Various Stoichiometries with BD.
Unaged Prepolymer at 200F. Uncatalyzed BD.



Partial Durometric Profiles of Vibrathane 8011 Cured with 3/1 TMP/TIPA at Various Temperatures and Stoichiometries.

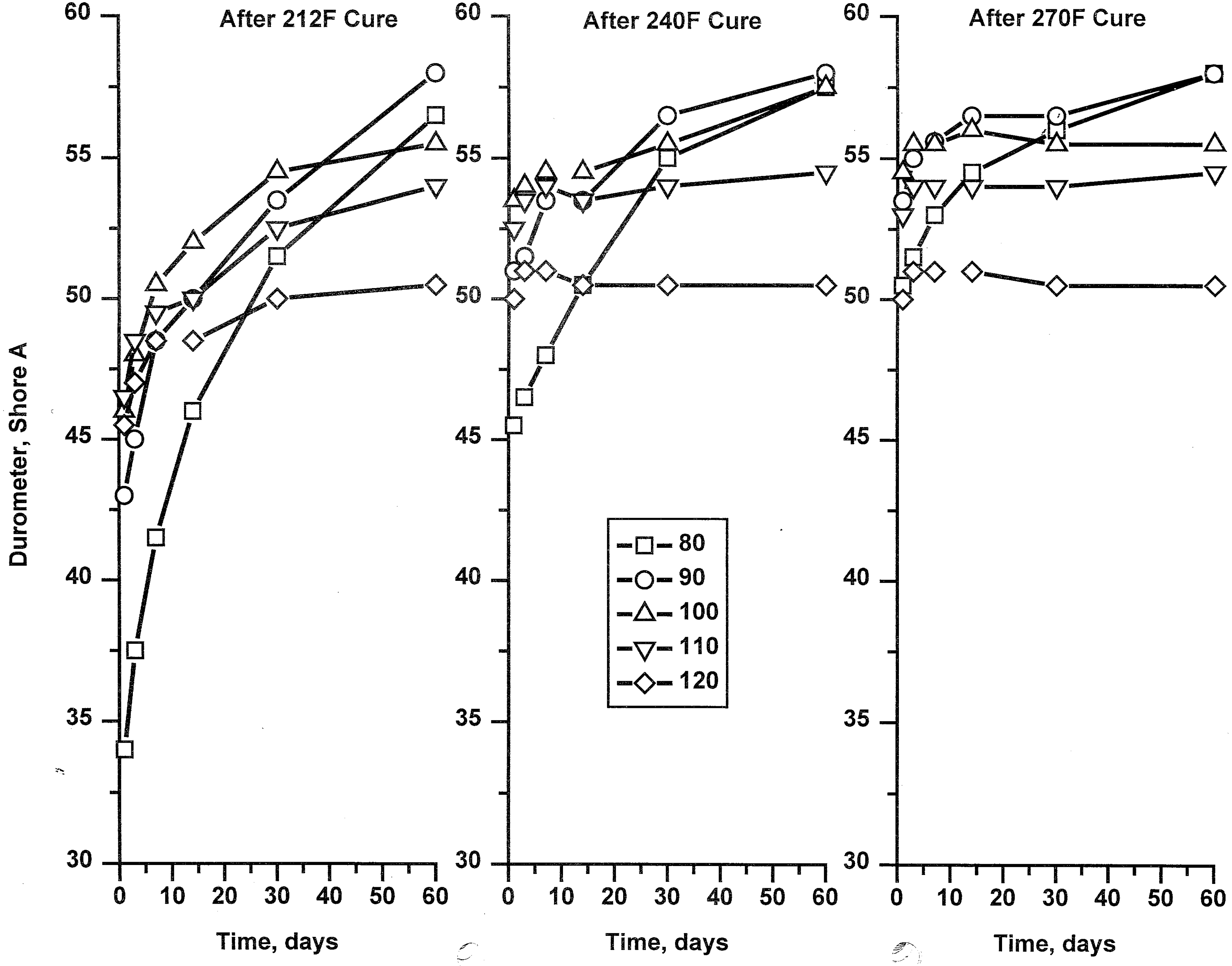


Figure 8

Durometric Profile of Unknown #1, a 6.3%NCO PTMG/MDI Prepolymer Cured at Unknown Temperature, Stoichiometry, Prepolymer Temperature, and Catalyst Level.

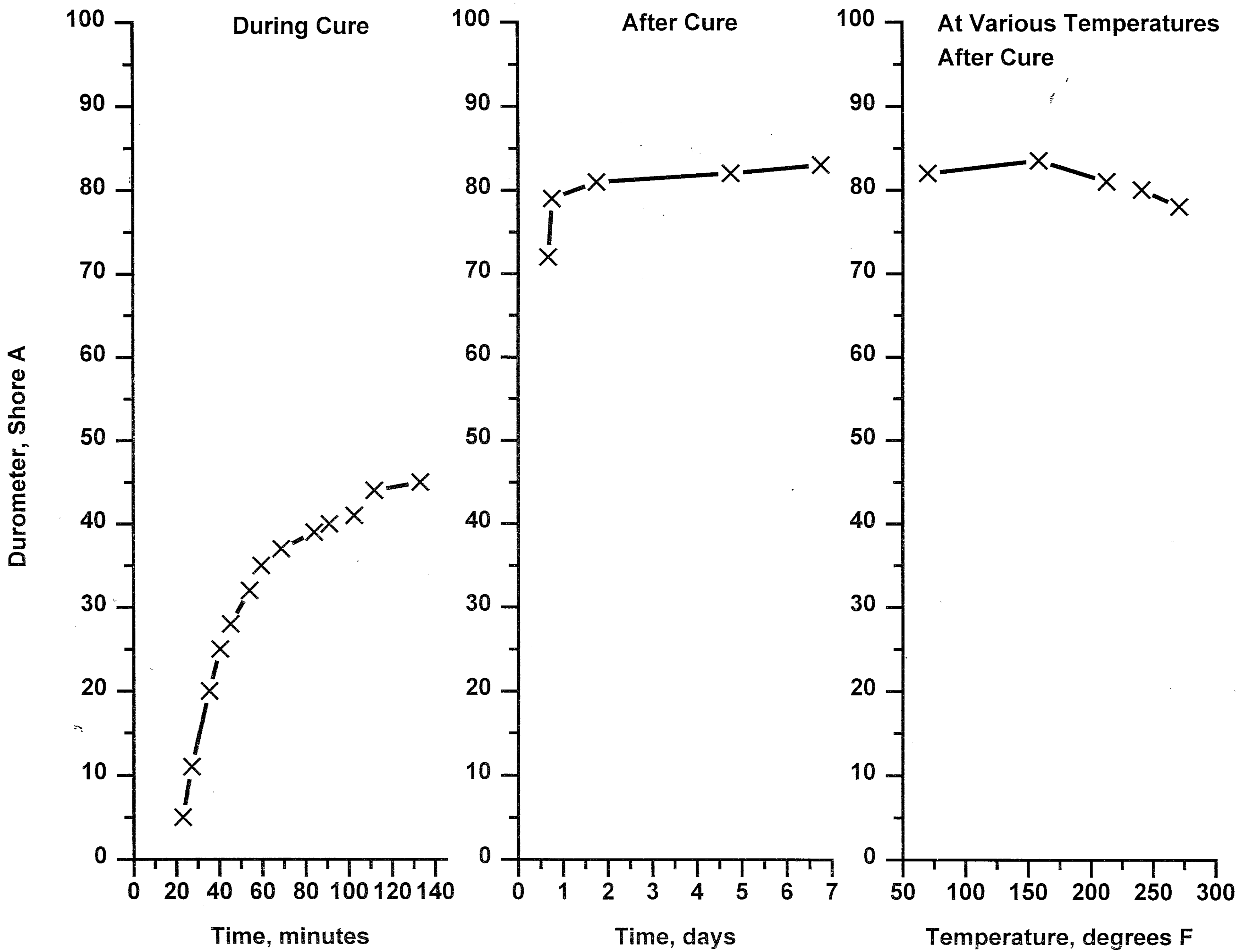


Figure 9

Durometric Profile of Unknown #2, a 6.3%NCO PTMG/MDI Prepolymer Cured at Unknown Temperature, Stoichiometry, Prepolymer Temperature, and Catalyst Level.